Accepted Manuscript

Synthesis and characterization of new electron acceptor perylene diimide molecules for photovoltaic applications

Erika Kozma, Dariusz Kotowski, Marinella Catellani, Silvia Luzzati, Antonino Famulari, Fabio Bertini

PII: S0143-7208(13)00176-9

DOI: 10.1016/j.dyepig.2013.05.011

Reference: DYPI 3948

To appear in: Dyes and Pigments

Received Date: 16 April 2013

Revised Date: 8 May 2013

Accepted Date: 14 May 2013

Please cite this article as: Kozma E, Kotowski D, Catellani M, Luzzati S, Famulari A, Bertini F, Synthesis and characterization of new electron acceptor perylene diimide molecules for photovoltaic applications, *Dyes and Pigments* (2013), doi: 10.1016/j.dyepig.2013.05.011.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Synthesis and characterization of new electron acceptor perylene diimide molecules for photovoltaic applications

Erika Kozma^{*a}, Dariusz Kotowski^a, Marinella Catellani^a, Silvia Luzzati^a, Antonino Famulari^b, Fabio Bertini^a

^aIstituto per lo Studio delle Macromolecole - Consiglio Nazionale delle Ricerche, 20133 Milano – Italy

^bPolitecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Via Mancinelli 7, 20131 Milano, Italy

*Corresponding author. Tel +39.02.23699.739 ; Fax: +39.02.70636.400 e-mail: <u>erika.kozma@ismac.cnr.it</u>

Abstract

Two new perylene diimide molecules, 1, 7-bis(1-naphtyl)-N,N'-bis-(10-nonadecyl)-perylene-3,4,9,10-bis (dicarboximide) **PDI-2** and 1,7-bis(5-acenaphtenyl)-N,N'-bis-(10-nonadecyl)-perylene-3,4,9,10-bis(dicarboximide) **PDI-3** have been synthesized and used as acceptor components in P3HT/PDI bulk heterojunction solar cells. The introduction of fused aromatic rings into the bay positions of the perylene core creates a stong steric hindrance, twisting the perylene plane with a direct consequence on the π - π intramolecular interactions between the adjacent PDIs. All these features contribute to the reduction of molecular aggregation in the solid state, with a strong influence on the performances of P3HT/PDI photovoltaic devices.

Keywords: perylene diimides, electron acceptor, organic solar cell, DFT calculations, HOMO and LUMO orbitals

Graphical abstract

Highlights

- Two new perylene diimide molecules were synthesized
- PDI-2 and PDI-3 were used as n-type components in solar cells
- Solar cells with P3HT exhibit efficiencies approaching 1%

1. Introduction

The harvest of energy directly from sunlight using photovoltaic technology is one of the main way to address the environmental issues of sustainable energy production from renewable sources. In recent years, organic photovoltaic devices have earned considerable research interest for the exploitation of solar energy in a sustainable, ecological friendly and cost-effective way. Organic solar cells are made with non-toxic and cheap materials and are manufactured by low energy technologies such as solution processing or roll-to-roll process on large areas of lightweight flexible substrates [1].

In organic solar cells the photoelectric conversion is based on the photoinduced electron transfer process involving two semiconducting materials with different ionization potential and electron affinity. The active layer in these bulk heterojunction devices (BHJ) is a bicontinuous interpenetrating network made of an electron-donor and an acceptor material: usually a π -conjugated polymer or molecule and a soluble, electron withdrawing fullerene derivative.

Although various conjugated organic materials, either molecules [2] or polymers [3], have been explored as electron donors and p-type semiconductors in organic solar cells, not so many electron acceptors, n-type semiconductors besides fullerenes have been used [4]. The fullerene derivatives are the dominant acceptors in organic photovoltaics, as they are characterized by outstanding electron affinity and ability to transport charge effectively. However, they are non-ideal materials because of their weak absorption properties and high commercial value, which is a significant drawback in industrial applications [5]. Thus, the development of alternative acceptor materials that exhibit favourable electron transport properties and good absorption over the visible range is very important. Perylene diimide (PDI) based polymers and molecules are suitable candidates as acceptor components in organic solar cells. In particular, the PDI molecules have been often used in dye-sensitized solar cells [6] and in vacuum deposited bilayer solar cells [7], rather than for BHJ photovoltaic devices [8].

Perylene diimide molecules, in addition to exceptional thermal, photochemical stability and significant charge transport properties [9], exhibit large optical absorption in the visible to near-infrared spectral region and irradiate fluorescence with quantum yields near unity. Despite such promising prospective, the photovoltaic parameters of solution processed bulk heterojunction solar cells that use PDI molecules are far below the theoretically expected values.

Several research groups have explored the reason of these low efficiencies of PDI based solar cells. A number of studies have been devoted to elucidate charge photogeneration in polymer/PDIs devices [10,11]. It was found that the photovoltaic conversion is limited by the aggregated PDI domains, which are acting as exciton traps [10]. Therefore, the design of perylene based molecules

should be oriented to create structures with relatively reduced π - π stacking, which contributes to the formation of smaller domains, and thus, to larger donor-acceptor interface area, allowing excitons to quickly reach a heterojunction.

Recently, a perylene diimide molecule containing alkyl substituents, both at the imide position and 2,5,8,11-core positions, used in blend with P3HT gave an efficiency of 0.5% [12]. It was suggested that the bulky alkyl side chains present on the PDI core reduce the π - π interactions between the perylene planes, leading to an improvement of the photovoltaic parameters in comparison with the unsubstituted perylene diimide [15].

Since PDI is well know as a chemically versatile building block whose properties, such as solidstate packing or HOMO and LUMO energy levels, which can be easily and specifically tailored either by introduction of the appropriate substituents at the imide positions [13] or perylene core positions [14]. Usually, the N-position of the PDIs are substituted with alkyl chains, preferably branched, in order to get high solubility of the material, whereas the core positions are available for many functional groups.

Using this possibility to tune PDI properties, we have designed two new electron-acceptor molecules for BHJ solar cell application with a reduced molecular aggregation in the solid state. To reach this goal the molecules should have a limited self-organization tendency, unusual for PDI derivatives, and weak intramolecular interactions via π - π stacking.

The substitution in bay positions of PDI with chemical groups having high steric hindrance can hamper the intermolecular approach of adjacent chromophores lowering or preventing the π - π noncovalent interactions. We have chosen two electron-rich fused aromatic rings, naphthalene and acenaphtene, as bay substituent groups. The steric hindrance of these groups induces a distortion of the perylene core and impedes the formation of intramolecular π - π stackings.

In this paper we present the synthesis and the characterization of two new PDI molecules: 1, 7-bis(1-naphtyl)-N,N'-bis-(10-nonadecyl)-perylene-3,4,9,10-bis(dicarboximide) (**PDI-2**) and 1, 7-bis(5-acenaphtenyl)-N,N'-bis-(10-nonadecyl)-perylene-3,4,9,10-bis(dicarboximide) (**PDI-3**) (see Scheme 1). Both PDIs have been used as acceptor components in bulk-heterojunction solar cell with P3HT. The photophysical and device properties of **PDI-2** and **PDI-3** have been compared with those of un-substituted **PDI-1** parent compound [15], which has long alkyl branched chains at the N-terminal positions and no substituents on the aromatic core.

2. Experimental

2.1. Materials and instruments

10-nonadecanone was purchased from TCI Europe. Sodium bis(2-methoxyethoxy) aluminium hydride (RedAl), perylene-3,4,9,10-tetracarboxylic dianhydride, naphtalene-1-boronic acid, acenaphtene-5-boronic acid, tetrakis(triphenylphosphine)palladium(0) were purchased from Aldrich and used as received without further purification. Solvents and reagents were dried and/or distilled by the usual methods and typically used under an inert gas atmosphere.

¹H-NMR spectra were recorded on a 400 MHz Bruker spectrometer operating at 11.7 T. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA 7 instrument with a platinum pan using 1.5 mg of material as probe. Before performing TGA run, the sample was held at 150 °C for 1 h; the scans were carried out from 50 up to 700 °C at heating rate of 10 °C min⁻¹ in a nitrogen atmosphere at a flow rate of 35 ml min⁻¹. Differential Scanning Calorimetry (DSC) measurements were carried out on a Perkin-Elmer Pyris 1 instrument equipped with a liquid nitrogen device. The sample, typically 2-3 mg, was placed in a sealed aluminum pan and the measurements were carried out from 0 to 200 °C under helium atmosphere using heating and cooling rates of 10 °C min⁻¹.

Cyclic voltammetry measurements were performed in solid state, under nitrogen atmosphere with a computer controlled Amel 2053 (with Amel 7800 interface) electrochemical workstation in a three electrode single-compartment cell using platinum electrodes and SCE as standard electrode, with Fc/Fc^+ redox couple as internal standard, with a tetrabutylammonium tetrafluoroborate solution (0.1M) in acetonitrile at a scan rate of 50mV/s.

Electronic absorption spectra were performed with a Perkin Elmer Lambda 9 spectrophotometer on chloroform solutions or spin coated films on quartz.

Photoluminescence (PL) spectra of PDIs and their blends with P3HT were recorded using 488 nm light excitation from a xenon lamp and a monochromator coupled to a N_2 cooled CCD detector.

2.2. Synthesis

Scheme 1 outlines the synthesis of compounds PDI-1, PDI-2 and PDI-3.

Scheme 1. Synthetic route toward PDI-1, PDI-2 and PDI-3

2.2.1. 10-Nonadecanamine

10-nonadecanamine was obtained according to the literature procedure [16]. Briefly, a solution of 500 mg (1.77 mmoles) of 10-nonadecanone in 5 ml of ethanol and 3 ml of pyridine was treated with 250 mg (3.6 mmoles) of hydroxylamine hydrochloride and then refluxed for 2 hours. The resulting mixture was then concentrated by evaporation and the residue was partitioned between 5% HCl and hexane. The organic layer was then washed several times with water, dried over MgSO₄ and concentrated to yield 480 mg of 10-nonadecanone oxime as an oil (91% yield). The oxime was then dissolved in 10 ml of dry toluene and 2 ml of 70% sodium bis(2-methoxyethoxy)aluminium hydride (RedAl) in toluene were dropwise added. There is an important gas evolution as the reductive agent is added which requires a particular attention when the reaction is carried out. The reaction mixture was refluxed for 2 hours, then cooled to the room temperature and carefully added to 10 ml of 5% HCl. At the end an additional quantity (3-4 ml) of concentrated HCl was added in order to dissolve the aluminium salts. The solution was extracted with hexane, washed with 5% NaOH solution, water and then dried over MgSO₄. After the evaporation of the solvent were obtained 408 mg of 10-nonadecanamine (89%). ¹H-NMR (CDCl₃): δ 0.81 (t, 6H), 1.20 (m, 32H), 2.14 (br, 2H), 2.68 (m, 1H). IR (KBr, cm⁻¹): ν 3372, 3256, 2494, 1463, 1377, 801, 727

2.2.2. N, N'-bis-(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide PDI-1

N, N'-bis-(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide was obtained by a modified procedure from the literature [16]. The condensation reaction of 3,4,9,10-perylenetetracarboxylic dianhydride (606 mg, 1.55 mmol) and 10-nonadecanamine (1.07 g, 3.78 mmol) was accomplished by conducting the imidazation reaction in the presence of zinc acetate (214 mg, 1.16 mmol) in quinoline (5 ml) at 160 °C for 4 hours under nitrogen atmosphere. The resulting N, N'-bis-(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide was isolated in 78% yield as a deep red solid after a silica gel column chromatography purification (hexane:CHCl₃=8:2 as eluent).

¹H-NMR (CDCl₃): δ 0.83 (t, 12H), 1.21 (m, 56H), 1.85 (m, 4H), 2.26 (m, 4H), 5.25 (m, 2H), 8.51 (br, 4H, pery-H), 8.59 (br, 4H, pery-H). IR (KBr, cm⁻¹): υ 2922, 2853, 1694, 1649, 1593, 1465, 1404, 1344, 1254, 1175

2.2.3. 1,7-dibromo-N,N'-bis(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide

1,7-dibromo-N,N'-bis(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide was obtained as described in literature [17]. A mixture of N,N'-bis(nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide (100 mg, 0.108 mmol), bromine (1184 mg, 7.4 mmol) in 2 ml CH₂Cl₂ was stirred at 60 °C in a closed vial for 4 hours. The reaction mixture was allowed to reach the

room temperature and then, after removing the excess of bromine by air bubbling, the solvent was removed under vacuum. The crude product was purified by a silica gel column chromatography, using hexane:CHCl₃=6:4 as eluent. The first band was collected to afford dibromo-N,N'-bis(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic diimide (as a mixture of 1,7-dibromo and 1,6-dibromo derivative 3:1) as a deep orange solid (108 mg, 92%). ¹H-NMR (CDCl₃): δ 0.85 (t, 12H), 1.25 (m, 56H), 1.85 (m, 4H), 2.25 (m, 4H), 5.20 (m, 2H), 8.70 (br, 2H, pery-H), 8.91 (br, 2H, pery-H), 9.52 (d, 2H, pery-H). IR (KBr, cm⁻¹): v 2919, 2849, 1700, 1660, 1589, 1465, 1382, 1327, 1237

2.2.4. 1, 7-bis(1-naphtyl)-N,N'-bis-(10-nonadecyl)-perylene-3,4,9,10-bis(dicarboximide) PDI-2

A mixture of 1,7-dibromo-N,N'-bis(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic diimide and naphthalene-1-boronic acid (2.04 equivalents) were dissolved in dry toluene (5 ml each 0.25 mmol of dibromo-N,N'-bis(nonadecyl)perylene-3,4,9,10-tetracarboxylic diimide) and 2M K₂CO₃ solution (1 ml each 4 ml of toluene). Catalytic amounts of Pd[PPh₃]₄ were added and the reaction mixture was stirred at 100 °C for 18 hours. Shortly after the addition of the catalyst, the colour of the mixture starts to change. At the end of the reaction time, the solution was cooled to room temperature, extracted with CHCl₃, washed with water, extracted and dried over MgSO₄ anh. concentrated to a smaller volume and dropped into methanol. The precipitate was filtered, and further purified by column chromatography, using hexane/CHCl₃ 3:2 as eluent.

1, 7-bis(1-naphtyl)-N,N'-bis-(10-nonadecyl)-perylene-3,4,9,10-bis(dicarboximide) PDI-2 was obtained as a deep red solid in 78% yield. ¹H-NMR(CDCl₃, 400MHz): $\delta = 8.64$ (2H, m, pery), 8.00 (4H, dd, pery), 7.62 (6H, m, naph), 7.52 (4H, t, naph), 7.31 (4H, t, naph), 5.10 (2H, m, -CH-N), 2.20 (4H, m, -CH₂-), 1.80 (4H, m, -CH₂-), 1.22 (56H, m, -CH₂-), 0.81 (12H, t, -CH₃).

2.2.5. 1,7-bis(5-acenaphtenyl)-N,N'-bis-(10-nonadecyl)-perylene-3,4,9,10-bis(dicarboximide) PDI-3

A mixture of 1,7-dibromo-N,N'-bis(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic diimide and acenaphthene-5-boronic acid (2.04 equivalents) were dissolved in dry toluene (5 ml each 0.25 mmol of dibromo-N,N'-bis(nonadecyl)perylene-3,4,9,10-tetracarboxylic diimide) and 2M K₂CO₃ solution (1 ml each 4 ml of toluene). Catalytic amounts of Pd[PPh₃]₄ were added and the reaction mixture was stirred at 100 °C for 18 hours. Shortly after the addition of the catalyst, the colour of the mixture starts to change. At the end of the reaction time, the solution was cooled to room temperature, extracted with CHCl₃, washed with water, extracted and dried over MgSO₄ anh. concentrated to a smaller volume and dropped into methanol. The precipitate was filtered, and further purified by column chromatography, using hexane/CHCl₃ 3:2 as eluent.

1, 7-bis(5-acenaphtenyl)-N,N'-bis-(10-nonadecyl)-perylene-3,4,9,10-bis(dicarboximide) PDI-3 was obtained as a deep violet solid in 63% yield. ¹H-NMR (TCE, 400MHz): δ =8.61 (2H, m, pery), 7.90 (4H, m, pery), 7.58 (2H, m, acenaph), 7.35 (4H, m, acenaph), 7.25 (4H, m, acenaph), 5.05 (2H, m, -CH-N), 3.45 (8H, m, -CH₂- acenaph), 2.05 (4H, m, -CH₂-), 1.73 (4H, m, -CH₂-), 1.12 (56H, m, -CH₂-), 0.78 (12H, t, -CH₃).

2.3. Device fabrication

Solar cells were made with the conventional geometry glass/ITO/PEDOT-PSS/P3HT:PDIs/Ca/Al in a MBraun drybox. The active layers were spin-coated from chlorobenzene or o-dichlorobenzene solution of P3HT:**PDI** (20 mg/ml or 25 mg/ml), with a thickness of about 100 nm. When chlorobenzene was used, after the deposition of the active layer a thermal annealing at different temperatures has been done, prior to the cathode deposition. In the case of o-dichlorobenzene, after the deposition, the active layer was solvent annealed by slow drying under a Petri dish (about 10 hours). After that, a mild thermal treatment of 90 °C/5 min has been done to remove the residual solvent.

The current density–voltage measurements were performed directly in the glove box where the cell was assembled and annealed, with a Keithley 2602 source meter, under a 1 sun, AM1.5G spectrum obtained from an ABET Technologies solar simulator. EQE spectral responses were recorded by dispersing a Xe lamp through a monochromator, using a Si solar cell with calibrated spectral response to measure the incident light power intensity at each wavelength. The devices were taken outside the glove box for the EQE measurements, after mounting them on a sealed cell to avoid moisture and oxygen exposure.

3. Computational details

A computational study was carried out on structures and energies of **PDI-1**, **PDI-2** and **PDI-3** molecules. To reduce the size of the conformational space, the alkyl branched chains at the imide positions have been replaced by methyl groups. All calculations were performed with the GAMESS-US suite of programs [18]. Stable low energy conformations were obtained by density functional theory (DFT) calculations [19]. In particular, the Becke's three parameter gradient-corrected hybrid functional (B3LYP) [20] together with the polarized standard 6-31G** basis set [21] were adopted. In order to scan properly the potential energy surfaces, different starting guess geometries were considered for the molecules under investigation. Full minimizations were carried out at the B3LYP/6-31G** level of the theory without imposing symmetry constrains. A vibrational analysis was performed at the same level of the theory on optimised geometries, where a lack of

imaginary frequencies confirmed that they represent minimum-energy structures. HOMO and LUMO orbitals have been plotted by McPlot program [22].

4. Results and discussion

4.1. Synthesis and thermal characterization

Two new perylene diimide molecules were synthesised through Suzuki coupling reaction. These molecules are soluble in common organic solvents, such as chloroform, dichloromethane, THF, toluene.

It is known that perylene derivatives with symmetrical and unsymmetrical alkyl side chains at the N-terminal position and no substituents on the aromatic core possess excellent thermal stability with high decomposition temperatures [23]. In particular, the TGA thermogram of **PDI-1** was reported in literature [15] and the molecule resulted stable up to 395 °C and then lost the nonadecyl groups attached to nitrogen atoms. The thermal stability of the novel PDIs molecules having fused aromatic substituents in the bay positions of the perylene core, was determined by TGA considering the onset of thermal decomposition, i.e. the temperature corresponding to initial 5% of weight loss. TGA traces reported in Fig. 1 show that **PDI-2** and **PDI-3** are thermally stable in inert atmosphere up to 400 °C. At higher temperatures both perylene derivatives show a fast weight loss with a maximum rate at 450 °C. The main degradation stage ends at around 500 °C and the residue yield calculated at 700 °C is ca. 40 wt. % for both molecules. However, the residue disappears when exposed to air atmosphere.

Figure 1. TGA curves of PDI-2 (—) and PDI-3(—) under inert atmosphere

The thermal behavior of the perylene diimide molecules was studied in the bulk by DSC analysis. The thermal analyses of the PDIs are reported in Figure 2, where successive scans, i.e. the cooling and the second heating, are displayed. The comparison between the thermograms clearly evidences the effect of the core substitution with fused aromatic rings on the thermal behavior of perylene diimide derivatives. The cooling run of **PDI-1** shows an exothermic transition centered at 81 °C, while the subsequent heating scan displays an endothermic peak at 99 °C with a heat flow of 9 J/g due to the crystal melting [16, 24]. Conversely, DSC scans carried out in the temperature range 0-200 °C at 10 °C/min of the molecules **PDI-2** and **PDI-3** do not show any thermal event. Thus, the presence of bulky substituents in bay position hinders the crystallization capability of the branched long alkyl side chains.

Figure 2. DSC scans of PDI-1 (—), PDI-2 (—) and PDI-3 (—) from cooling (dashed line) and second heating (solid line) cycle.

4.2. Electrochemical properties

The electrochemical properties of **PDI-2** and **PDI-3** films were investigated by cyclic voltammetry (CV). The CV curve was recorded vs the potential of SCE reference electrode, using ferrocene as internal standard. As shown in Fig.3, the half way reduction potentials ($E_{red}^{1/2}$) for **PDI-2** and **PDI-3** are -0.67 eV and -0.77 eV respectively. From the empirical formulas E_{LUMO} =-e($E_{red}^{1/2}$ +4.4 eV) and $E_{HOMO} = E_g^{opt} + E_{LUMO}$, the HOMO and LUMO energy levels of **PDI-2** can be calculated as -5.79 eV and -3.73 eV, while the HOMO and LUMO energy levels of **PDI-3** are -5.55 eV and -3.63 eV.

Figure 3. Cyclic voltammograms of PDI-2 and PDI-3 thin films

Table 1 summarizes these results (together with calculated properties, see next section) showing that the energy levels are slightly changed and the optical energy gap decreased with respect to **PDI-1**. Since the HOMO and LUMO energy levels reported in the literature for P3HT are typically -5.0 eV and -3.0 eV, it is clear that the HOMO and LUMO energy levels of PDIs are suitable to drive efficiently exciton dissociation at the P3HT/PDIs heterojunction interfaces.

 Table 1. Electrochemical characteristics, experimental and calculated HOMO-LUMO values and optical energy band gaps for PDI-1, PDI-2 and PDI-3

4.3 Theoretical calculations

The ground-state geometries and electronic structures of PDIs molecules were obtained at the B3LYP/6-31G** level. This study provided preliminary insights into the electronic structures and interactions in these molecular systems. As expected, it was confirmed that, with no substituents in the bay positions, the **PDI-1** core is nearly planar. According to the calculations, the absolute minima obtained for both **PDI-2** and **PDI-3** systems show that the bay-substitutions introduce a twisting of the two naphthalene subunits in the perylene core around 19°, thus causing a reduced planarity and rigidity of the perylene. The dihedral angles between the perylene plane and the

substituent moieties were determined to be 55° and 63° for **PDI-2** and **PDI-3**, respectively (see Figure 4).

Figure 4. Optimized structures of PDI-2 (a) and PDI-3 (b) obtained by DFT calculations at the B3LYP/6-31G** level.

The electron distribution of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of ground-state optimized structures for **PDI-2** and **PDI-3** systems are illustrated in Figure 5; the corresponding energies are summarized in Table 1.

Figure 5. Molecular orbital surfaces of the HOMO (bottom) and LUMO (top) of **PDI-2** (a) and **PDI-3** (b) molecules obtained by DFT calculations at the B3LYP/6-31G** level.

For both systems, because of the π -conjugation, the electron distribution of the HOMOs was found to be delocalized over the entire molecule, while the electron distribution of the LUMOs were found to be predominantly located on the perylene core. This outcome indicates that in the excitation process from HOMO to LUMO energy levels, a charge is transferred from the substituent units to the central perylene acceptor moiety. The calculated HOMO and LUMO energy levels of groundstate optimized geometries for compounds **PDI-1**, **PDI-2** and **PDI-3** and corresponding gaps, estimated by using the differences between the HOMO and LUMO energies (Δ HL), are in concordance with the experimental trend.

4.4. Optical properties

The UV-Vis absorption spectra of **PDI-1**, **PDI-2** and **PDI-3** in solution and in film, along with the molar extinction are shown in Fig. 6.

In the absence of any substituent in the bay positions, **PDI-1** core is nearly planar and the optical properties are significantly different in solution and in solid state. Generally, in solution, the PDIs are characterized by two absorption bands which are assigned to the 0-0 and 0-1 electronic transitions. Passing from solution to solid state, the relative intensity of these absorption bands reverses, the spectra become more broadened and there is a loss of the fine vibronic structure. This is an indication that the PDIs molecular scaffolds allow π - π intermolecular interactions, inducing molecular aggregation [9].

PDI-2 and **PDI-3** in chloroform solution exhibit absorption in the visible range with peak maxima at 542 nm and 558 nm. Interestingly, the absorption maxima and its features do not alter with the concentration and remain unchanged passing from solution to solid state. This is an unusual behaviour for perylene diimide systems, since it is well known that the π - π intramolecular interactions have a strong influence on PDI optical properties.

PDI-2 and **PDI-3** have been designed with this purpose: the long alkyl branched chains at the imide positions assure a high solubility, while the fused aromatic rings lead to a twisted perylene plane and create a strong steric hindrance. These effects decrease the π - π stacking and lead almost to an isolation of the π systems in the solid state. Up to now, this isolation process was observed only for bay position tetrasubstituted perylenes [12,25].

Figure 6. Normalized absorption spectra of PDIs in solution (dash line) and solid state (solid line) and molar extinctions for PDIs in 1.25x10⁻⁴M solutions in CHCl₃

By making a comparison between the UV-Vis spectra for thin films and solutions of **PDI-2** and **PDI-3**, there is only a relatively small shift of 5 and 1 nm, respectively, indicating very weak intermolecular interactions between the chromophores in the film. The spectroscopic feature of **PDI-2** and **PDI-3** can be associated to the twisted nature of the perylene core evidenced by the theoretical calculations.

Figure 7. Normalized fluorescence spectra of PDIs in solution (dash line) and solid state (solid line)

The photoluminescence (PL) spectra shown in figure 7 bring further evidences which prove the above findings. The PL spectrum of **PDI-1** film has a broad, vibronic free, batochromic shifted band (about 80 nm) with respect to the solution. The red shift around 615 nm is a result of the optical excitation of the perylene diimide aggregates which activates the excimer species [26]. In contrast, the PL spectra of **PDI-2** and **PDI-3**, in solution and film are substantially identical suggesting the absence of any strong π - π interactions.

4.5. Photovoltaic properties

The photovoltaic properties of **PDI-1**, **PDI-2** and **PDI-3** were investigated in bulk heterojunction solar cells, with P3HT as donor, having ITO/PEDOT:PSS/P3HT:PDIs/Ca/Al structure. Chlorobenzene (CB) and o-dichlorobenzene (DCB) were chosen as processing solvents due to their good solvation properties and low evaporation rates.

The P3HT/**PDI-1** blends were first deposited from o-dichlorobenzene, but this procedure yielded active layer with extended phase segregation and **PDI-1** microcrystallites. To lower the phase segregation and to improve the bicontinuous film structure, P3HT/**PDI-1** blends were deposited from chlorobenzene. **PDI-2** and **PDI-3** were deposited from o-dichlorobenzene and have shown good processability in blend with P3HT forming active layers with no phase segregation visible by optical microscopy.

Table 2 and 3 show the device performances under the illumination of AM 1.5G solar irradiance (100mW/cm²). The photovoltaic characteristics of P3HT/PDIs as-cast devices with different blend composition are summarized in Table 2.

The PV characteristics of P3HT/**PDI-1** devices are in agreement with previously reported results obtained with an analogous PDI [15]. The low performances of **PDI-1** solar cells are related to the high tendency of PDIs to crystallize in blends with polymers, leading to large scale segregations [8,26]. In all cases, the photovoltaic performances of **PDI-2** and **PDI-3** based solar cells are better in comparison with those based on **PDI-1**. Moreover, such trend of the photovoltaic parameters of P3HT/**PDI-2** and P3HT/**PDI-3** are irrespective from the device deposition or processing methods and can be correlated with the peculiar intermolecular π - π stacking of the two new PDIs.

 Tabel 2. Photovoltaic parameters for non annealed P3HT/PDI devices using different blend compositions deposited from chlorobenzene

The best performances were obtained for P3HT/PDI solar cells made with 1:2 weight ratio blends. Taking this blend composition as reference, different annealing treatments were done in order to optimize the device performances. It is well known that the polymer solar cells containing P3HT as donor component improve their efficiencies upon thermal or solvent annealing. These treatments change the morphology of the active layer inducing a better intermolecular alignment of the polymer chains that increase the hole mobility [27]. In our studies we have used the most common annealing conditions for P3HT based devices, performing different thermal or solvent treatments on the active layers. The results are summarized in Table 3.

It can be noticed that after thermal treatment the device photovoltaic parameters are improved with respect to the non annealed solar cells. For P3HT/**PDI-2** devices, after thermal annealing at 150 °C the PCE reaches 0.71%, while for P3HT/**PDI-3** solar cells the best performances of 0.82% were obtained using a thermal treatment at 120 °C.

Table 3. Photovoltaic parameters for P3HT/PDI 1:2 blends with different annealing conditions

We have also explored the use of solvent annealing prior to cathode deposition, by placing the P3HT/PDI coated substrates in a saturated o-dichlorobenzene atmosphere for 10 hours. Both solvent exposure and thermal annealing produce the increase of the photovoltaic performances respect to not annealed solar cells. The best PCEs were obtained for both **PDI-2** and **PDI-3** devices after solvent annealing with DCB for 10 hours.

Figure 8 shows the best device characteristics of P3HT/PDIs solar cells, with a 1:2 (w:w) donor/acceptor composition.

Figure 8. P3HT:PDIs (1:2 w:w) device characteristics. Left-IV curves under AM1.5 G solar simulation, at 100 mW/cm². Right-Incident photon to current efficiency spectra

Comparing **PDI-2** and **PDI-3** device parameters with those of **PDI-1** parent compound it can be noticed very clearly, that the introduction of the fused aromatic rings into the bay position of the perylene diimide core has a strong influence on photovoltaic performances. The blends nano-morphology, as probed from the PL measurements on the optimized active layers (Figure 9), suggest that phase segregation is more pronounced in **PDI-1** based respect to **PDI-2** and **PDI-3** devices.

Figure 9. Left- PL spectra of pristine component films (dashed lines) and optimized (1:2 w:w) P3HT:PDIs blends; Right- Absorption spectra of optimized P3HT:PDIs blends

It is possible to draw some correlation between the structure of the new PDI molecules and their operation in solar cells with P3HT on the basis of the spectroscopic experiments and the theoretical evidences previously discussed. The morphological characterization of P3HT:PDIs blend to discern the structural behaviour of these perylenes in the solid state will be presented elsewhere.

The IPCE and the Jsc of P3HT/**PDI-2** and P3HT/**PDI-3** devices drastically increase compared to **PDI-1** based solar cell. On the basis of the recorded UV-Vis absorption spectra of the active layers (Figure 9), it is reasonable to suppose that changes in absorption cross sections play a minor role for understanding the enhancement of the photocurrent in **PDI-2** and **PDI-3** based blend devices. The improvements of the photocurrents are thus related to the efficiencies of exciton harvesting at the P3HT/PDI interfaces, of charge photo-generation and collection to the electrodes.

The crystallization of PDI-2 and PDI-3 is nearly absent due to the lack of the π - π interactions, as suggested by the spectroscopical and computational studies, therefore exciton trapping should be diminished in the active layers [10]. Moreover, the photoluminescence spectra of the PDI-2 and PDI-3 blends (Figure 9) suggests a reduction of the P3HT/PDI nano-phase segregation. As a consequence, it is expected that in PDI-2 and PDI-3 blends the exciton harvesting yield is improved, thus contributing to the enhancement of photocurrent.

It was shown that small separation distances facilitate the formation of a stable CT state (CT exciton) leading to inefficient charge carrier separation [28]. In PDI-2 and PDI-3 molecules the π - π interaction was indeed heavily reduced by introducing the fused aromatic rings in bay positions, therefore in the P3HT blend the separation distance at the polymer/PDI is likely increasing. Accordingly, less bounded CT excitons should be formed, favouring the charge separation. Moreover, for PDI-2 and PDI-3, twisted structures are formed and a higher dimensionality is achieved in the polymeric blends, which can also lead to an increase of the charge separation at the donor-acceptor interface [29].

The FF parameter is also improving substantially from PDI-1 to PDI-2 and PDI-3 solar cells. This bring further support for a better charge carrier separation in PDI-2 and PDI-3 blend, and suggests a more effective and balanced charge carrier collection in these devices [30].

Finally, the reduction of the V_{OC} in **PDI-1**, compared to **PDI-2** and **PDI-3** based solar cells, is not justified by the corresponding LUMO energy levels of the acceptor molecules. It was proposed that in BHJ solar cells, the V_{oc} should scale to the energy position of the CT state [31]. Therefore, the observed reduction of the V_{oc} , in **PDI-1** solar cells, seems to be consistent to the previously suggested higher CT exciton binding energy in **PDI-1**, as compared to **PDI-2** and **PDI-3** blends.

5. Conclusions

In summary, we designed, synthesized and characterized two novel perylene diimides molecules, **PDI-2** and **PDI-3**, with fused aromatic rings on the perylene core. These materials possess interesting optical and structural features, revealing extremely weak π - π interactions between the

perylene planes, which is an interesting feature, since PDIs are well known for their strong intermolecular packing properties.

DFT calculations show that the bay-substitutions introduces a twisting of the perylene core and the fused aromatic rings form dihedral angles with the perylene plane of 55° and 63° for **PDI-2** and **PDI-3**, respectively. The optical absorption and emission properties of the two molecules show the same features in solution and in the solid state. These theoretical and optical evidences indicate the low tendency of the two PDI to form π - π stacking interactions, preventing the crystallization in the solid state and reducing the phase segregation in the polymeric blends with P3HT.

Bulk heterojunction P3HT/PDIs solar cells were prepared and their photovoltaic performances were measured as a function of both the active layer composition and the annealing device condition. Photovoltaic efficiencies approaching 1% were found for **PDI-2** and **PDI-3** based solar cells.

Acknowledgements

This work has been supported by the E.U. Marie Curie Reintegration project grant "DAMASCO" FP7-PEOPLE-2010-RG-268229, by the Fondazione Cariplo (project "PLENOS", Ref 2011-0349) by Accordo Quadro between Regione Lombardia and CNR – Cluster Project 'Energy' n° 17348, by Regione Lombardia and CILEA-CINECA through a LISA Initiative (Laboratory for Interdisciplinary Advanced Simulation) 2012 grant.

References

[1] (a) Parida B, Iniyan S, Goic R. A review of solar photovoltaic technologies. Renew Sust Energ Rev 2011;15:1625-36.

(b) Myers JD, Xue J Organic Semiconductors and their Applications in Photovoltaic Devices. Polym Rev 2012;52:1–37

[2] Mishra A, Bäuerle P. Small Molecule Organic Semiconductors on the Move:

Promises for Future Solar Energy Technology. Angew Chem Int Ed 2012;51:2020-67

[3] (a) Cheng YJ, Yang SH, Hsu CS. Synthesis of conjugated polymers for organic solar cell applications. Chem Rev 2009;109:5868-923;

(b) Zhou H, Yang L, You W. Rational Design of High Performance Conjugated Polymers for Organic Solar Cells. Macromolecules 2012;45:607-32

[4] Zhao X, Zhan X. Electron transporting semiconducting polymers in organic electronics. Chem Soc Rev 2011;40:3728-43

[5] Dennler G, Scharber MC, Brabec C J. Polymer-Fullerene Bulk-Heterojunction Solar Cells. Adv Mater 2009;21:1323-38

[6] Ferrere S, Gregg B A. New perylenes for dye sensitization of TiO₂. New J Chem 2002;26:1155-60

[7] Tettignies R, Nicolas Y, Blanchard P, Levillain E, Nunzi JM, Roncali J. Planarized Star-Shaped Oligothiophenes as a New Class of Organic Semiconductors for Heterojunction Solar Cells. Adv Mater 2003;15:1939-43

[8] (a) Dittmer J J, Marseglia E A, Friend R H. Electron Trapping in Dye/Polymer Blend Photovoltaic Cells. Adv Mater 2000;12:1270-4;

(b) Neuteboom EE, Meskers SKJ, Van Hal PA, Van Duren J KJ, Mejner EW, Janssen RAJ, et al. Alternating Oligo(p-phenylenevinylene)-perylene Bisimide Copolymers: Synthesis, Photo-physics, and Photovoltaic Properties of a New Class of Donor-Acceptor Materials. J Am Chem Soc 2003;125:8625-38;

(c) Liu Y, Yang C, Li Y, Li Y, Wang S, Zhuang J, et al. Synthesis and Photovoltaic Characteristics of Novel Copolymers Containing Poly(phenylenevinylene) and Triphenylamine Moieties Connected at 1,7 Bay Positions of Perylene Bisimide. Macromolecules 2005;38:716-21;

(d) Li C, Wonneberger H. Perylene Imides for Organic Photovoltaics: Yesterday, Today, and Tomorrow. Adv Mater 2012;24:613-636;

(e) Kozma E, Catellani M. Perylene diimides based materials for organic solar cells. Dyes and Pigments 2013;98:160-179.

[9] Huang C, Barlow S, Marder SR. Perylene-3,4,9,10-tetracarboxylic Acid Diimides: Synthesis, Physical Properties, and Use in Organic Electronics. J Org Chem 2011;76:2386-07.

[10] Howard IA, Laquai F, Keivanidis PE, Friend RH, Greenham NC. Perylene Tetracarboxydiimide as an Electron Acceptor in Organic Solar Cells: A Study of Charge Generation and Recombination. J Phys Chem C 2009;113:21225-32.

[11] Shoaee S, An Z, Zhang X, Barlow S, Marder SR, Duffy W, et al. Charge photogeneration in polythiophene-perylene diimide blend films. Chem Commun 2009:5445-7.

[12] Kamm V, Battagliarin G, Howard IA, Pisula W, Mavrinskiy A, Li C, et al., Polythiophene:Perylene Diimide Solar Cells - the Impact of Alkyl-Substitution on the Photovoltaic Performance. Adv Energy Mater 2011;1:297-02.

[13] Segura JL, Herrera H, Bäuerle P. Cyclic carboxylic imide structures as structure elements of high stability. Novel developments in perylene dye chemistry. J Mater Chem 2012;22:8717-33.

[14] (a) Würtner F, Stepanenko V, Chen Z, Saha-Möller CR, Kocher N, Stalke D. Preparation and characterization of regioisomerically pure 1,7-disubstituted perylene bisimide dyes. J Org Chem 2004;69:7933-9;

(b) Chen Z, Baumeister U, Tschierske C, Würtner F. Effect of core twisting on self-assembly and optical properties of perylene bisimide dyes in solution and columnar liquid crystalline phases. Chem Eur J 2007;13:450-65.

[15] Shin WS, Jeong HH, Kim MK, Jin SH, Kim MR, Lee JK, et al. Effects of functional groups at perylene diimide derivatives on organic photovoltaic device application. J Mater Chem 2006;16:384-390.

[16] Wescott LD, Mattern DL, Donor- σ -acceptor molecules incorporating a nonadecylswallowtailed perylenediimide acceptor, J Org Chem 2003;68:10058.

[17] Rajasingh P, Cohen R, Shirman E, Shimon LJW, Rybtchinski B, Selective bromination of perylene diimides under mild conditions, J Org Chem 2007;72:5973.

[18] (a) Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Su S, Windus TL, Dupuis M, Montgomery JA, General Atomic and Molecular Electronic Structure System, J Comput Chem 1993;14:1347-1363;

(b) Gordon MS, Schmidt MW, Theory and Applications of Computational Chemistry, the first forty years, C. E. Dykstra, G. Frenking, K. S. Kim, G. E. Scuseria (editors), Elsevier, Amsterdam, 2005, p. 1167-1189.

[19] (a) Parr RG, Yang W, Density Functional Theory of Atoms and Molecules, Oxford Scientific, 1989;

(b) Koch W, Holthausen MC, A Chemist's Guide to Density Functional Theory, Wiley VCH, 2001;(c) Jensen F, Introduction to Computational Chemistry, Wiley and Sons, Chichester, 2007.

[20] (a) Becke AD, Density-functional thermochemistry. III. The role of exact exchange , J Chem

Phys 1993;98:5648-5652;

(b) Stephens PJ, Devlin FJ, Chablonwski CF, Frisch MJ, Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields, J Chem Phys 1994;98: 11623-11627;

(c) Hertwig RH, Koch W, On the parameterization of the local correlation functional: What is Becke-3-LYP?, Chem Phys Lett 1997;268:345-351.

[21] (a) Ditchfield R, Hehre WJ, Pople JA, Self-Consistent Molecular-Orbital Methods. IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules, J Chem Phys 1971;54:724-728;

(b) Hehre WJ, Ditchfield R, Pople JA, Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. J Chem Phys 1972;56:2257-2261.

[22] Bode BM, Gordon MS, Macmolplt: a graphical user interface for GAMESS, J Mol Graphics and Modeling 1998;16:133-138.

[23] (a) Nolde F, Pisula W, Müller S, Kohl C, Müllen K. Chem Mater 2006;18:3715-25;

(b) Türkmen G, Eten-Ela S, Icli S. Dyes and Pigm 2009;83:297-303.

[24] Balakrishnan K, Datar A, Naddo T, Huang J, Oitker R, Yen M, Zhao J, Zang L. Effect of sidechain substituents on self-assembly of perylene diimide molecules: morphology control, J Am Chem Soc 2006;128:7390-8.

[25] (a) Arantes C, Scoltz M, Schmidt R, Dehm V, Rocco MLM, Schöll A, et al. Comparative analysis of the energy levels of planar and core-twisted perylene bisimides in solution and solid state by UV/VIS, CV, and UPS/IPES. Appl Phys A 2012;108:629-37

(b) Kaiser TE, Stepanenko V, Würtner F. Fluorescent J-Aggregates of Core-Substituted Perylene Bisimides: Studies on Structure–Property Relationship, Nucleation–Elongation Mechanism, and Sergeants-and-Soldiers Principle. J Am Chem Soc 2009;131:6719-32.

[26] Keivanidis PE, Howard IA, Friend RH, Intermolecular Interactions of Perylene diimides in Photovoltaic Blends of Fluorene Copolymers: Disorder Effects on Photophysical Properties, Film Morphology and Device Efficiency. Adv Funct Mater 2008;18:3189-02.

[27] Kim Y, Cook S, Tuladhar SM, Choulis SA, Nelson J, Durrant JR, Bradley DDC, et al. A strong regioregularity effect in self-organizing conjugated polymer films and high efficiency polythiophene-fullerene solar cells, Nat Mater 2006;5:197-203.

[28] Holcombe TW, Norton JE, Rivnay J, Woo CH, Goris L, Griffini G, et al. Steric Control of the Donor/Acceptor Interface: Implications in Organic Photovoltaic Charge Generation. J Am Chem Soc 2011;133:12106-14.

[29] (a) Gregg BA, Entropy of Charge Separation in Organic Photovoltaic Cells: The Benefit of Higher Dimensionality. J Phys Chem Lett 2011;2:3013-15;

(b) Clark TM, Durrant JR, Charge photogeneration in organic solar cells. Chem Rev 2010;110:6736-67.

[30] Lenes M, Morana M, Brabec CJ, Blom PW, Recombination-Limited Photocurrents in Low Bandgap Polymer/Fullerene Solar Cells. Adv Funct Mater 2009;19:1106-11.

[31] K. Vandewal, A. Gadisa, W. D. Oosterbaan, S. Bertho, F. Banishoeib, I. Van Severen, L.Lutsen, T. J. Cleij, D. Vanderzande, J. V. Manca, The relation between open circuit voltage and the onset of photocurrent genration by charge transfer absorption in polymer:fullerene bulk heterojunction solar cells, Adv Funct Mater 2008;18:2064-2070.

Synthesis and characterization of new electron acceptor perylene diimide molecules for photovoltaic applications

Erika Kozma^{*a}, Dariusz Kotowski^a, Marinella Catellani^a, Silvia Luzzati^a, Antonino Famulari^b, Fabio Bertini^a

^aIstituto per lo Studio delle Macromolecole - Consiglio Nazionale delle Ricerche, 20133 Milano – Italy

^bPolitecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta",

Via Mancinelli 7, 20131 Milano, Italy

*Corresponding author. Tel +39.02.23699.739 ; Fax: +39.02.70636.400

e-mail: erika.kozma@ismac.cnr.it



Scheme 1. Synthetic route toward PDI-1, PDI-2 and PDI-3



Figure 1. TGA curves of PDI-2 (—) and PDI-3(—) under inert atmosphere



Figure 2. DSC scans of PDI-1 (—), PDI-2 (—) and PDI-3 (—) from cooling (dashed line) and second heating (solid line) cycle.



Figure 3. Cyclic voltammograms of PDI-2 and PDI-3 thin films



Figure 4. Optimized structures of **PDI-2** (a) and **PDI-3** (b) obtained by DFT calculations at the B3LYP/6-31G** level.



Figure 5. Molecular orbital surfaces of the HOMO (bottom) and LUMO (top) of **PDI-2** (a) and **PDI-3** (b) molecules obtained by DFT calculations at the B3LYP/6-31G** level.



Figure 6. Normalized absorption spectra of PDIs in solution (dash line) and solid state (solid line) and molar extinctions for PDIs in 1.25×10^{-4} M solutions in CHCl₃



Figure 7. Normalized fluorescence spectra of PDIs in solution (dash line) and solid state (solid line)



Figure 8. P3HT:PDIs (1:2 w:w) device characteristics. Left-IV curves under AM1.5 G solar simulation, at 100 mW/cm². Right-Incident photon to current efficiency spectra



Figure 9. Left- PL spectra of pristine component films (dashed lines) and optimized (1:2 w:w) P3HT:PDIs blends; Right- Absorption spectra of optimized P3HT:PDIs blends

optical ci	nergy ba	nu gaps n	л і рі-і,	, I DI- 2 and	1 DI-3				
Sample	E_{red}^{0}	$E_{red}^{1/2}$	E_{red}^{p}	HOMO	LUMO	E_g^{opt}	HOMO ^a	LUMO ^a	ΔHL^{b}
	(V)	(V)	(V)	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)
PDI-1	-0.65	-0.73	-0.89	-5.79	-3.67	2.12	-5.96	-3.43	2.53
PDI-2	-0.61	-0.67	-0.75	-5.79	-3.73	2.06	-5.64	-3.28	2.36
PDI-3	-0.59	-0.77	-0.80	-5.55	-3.63	1.92	-5.47	-3.16	2.30

Table 1. Electrochemical characteristics, experimental and calculated HOMO-LUMO values and optical energy hand gaps for PDI-1 PDI-2 and PDI-3

 E_{red}^{0} -onset reduction potential; $E_{red}^{1/2}$ -halfway reduction potential; E_{red}^{p} -peak reduction potential; E_{g}^{opt} -optical energy band gap (calculated from the onset of the absorption in solid state)

^aB3LYP/6-31G** energies. ^bB3LYP/6-31G** HOMO-LUMO energy gaps.

$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	2/6-31G** energie 2/6-31G** HOM	5-31G** HOMO-LUMO energy gaps.						
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	Molecule	P3HT:PDI	$V_{OC}(V)$	FF	J _{SC}	PCE (%)		
PDI-11:1 0.29 0.30 $4x10^{-1}$ 0.03 1:2 0.43 0.38 $2.6x10^{-1}$ 0.04 PDI-21:1 0.49 0.33 2.16 0.35 1:2 0.55 0.39 1.95 0.42 2:1 0.47 0.30 1.56 0.22 PDI-31:1 0.46 0.25 2.50 0.28 1:2 0.68 0.35 1.38 0.33 2:1 0.45 0.26 1.70 0.20		(w:w)		\mathbf{Y}	(mA/cm^2)			
PDI-21:20.430.38 2.6×10^{-1} 0.04PDI-21:10.490.332.160.351:20.550.391.950.422:10.470.301.560.22PDI-31:10.460.252.500.281:20.680.351.380.332:10.450.261.700.20	PDI-1	1:1	0.29	0.30	$4x10^{-1}$	0.03		
PDI-2 1:1 0.49 0.33 2.16 0.35 1:2 0.55 0.39 1.95 0.42 2:1 0.47 0.30 1.56 0.22 PDI-3 1:1 0.46 0.25 2.50 0.28 1:2 0.68 0.35 1.38 0.33 2:1 0.45 0.26 1.70 0.20		1:2	0.43	0.38	2.6×10^{-1}	0.04		
1:2 0.55 0.39 1.95 0.42 2:1 0.47 0.30 1.56 0.22 PDI-3 1:1 0.46 0.25 2.50 0.28 1:2 0.68 0.35 1.38 0.33 2:1 0.45 0.26 1.70 0.20	PDI-2	1:1	0.49	0.33	2.16	0.35		
PDI-3 2:1 0.47 0.30 1.56 0.22 1:1 0.46 0.25 2.50 0.28 1:2 0.68 0.35 1.38 0.33 2:1 0.45 0.26 1.70 0.20		1:2	0.55	0.39	1.95	0.42		
PDI-3 1:1 0.46 0.25 2.50 0.28 1:2 0.68 0.35 1.38 0.33 2:1 0.45 0.26 1.70 0.20		2:1	0.47	0.30	1.56	0.22		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	PDI-3	1:1	0.46	0.25	2.50	0.28		
2:1 0.45 0.26 1.70 0.20		1:2	0.68	0.35	1.38	0.33		
		2:1	0.45	0.26	1.70	0.20		

Tabel 2. Photovoltaic parameters for non annealed P3HT/PDI devices using different blend compositions deposited from chlorobenzene

Molecule	Annealing	$V_{OC}(V)$	FF	J _{SC}	PCE (%)
	conditions			(mA/cm^2)	
PDI-1	$150^{\circ}C^{a}$	0.40	0.33	0.95	0.13
PDI-2	not annealed	0.55	0.39	1.95	0.42
	$120^{\circ}C^{a}$	0.56	0.43	2.28	0.55
	$150^{\circ}C^{a}$	0.57	0.53	2.35	0.71
	solvent ann ^b .	0.61	0.52	2.87	0.91
PDI-3	not annealed	0.68	0.35	1.38	0.33
	$120^{\circ}C^{a}$	0.67	0.47	2.60	0.82
	$150^{\circ}C^{a}$	0.58	0.52	2.02	0.61
	solvent ann ^b .	0.67	0.50	2.86	0.96

^a thermal annealing was made for 5 min after the deposition of the active layer from chlorobenzene; ^b o-dichlorobenzene (DCB) solvent annealed 10 hours

Table 3. Photovoltaic parameters for P3HT/PDI 1:2 blends with different annealing conditions

Synthesis and characterization of new electron acceptor perylene diimide molecules for photovoltaic applications

Erika Kozma^{*a}, Dariusz Kotowski^a, Marinella Catellani^a, Silvia Luzzati^a, Antonino Famulari^b, Fabio Bertini^a

^aIstituto per lo Studio delle Macromolecole - Consiglio Nazionale delle Ricerche, 20133 Milano – Italy

^bPolitecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Via Mancinelli 7, 20131 Milano, Italy

*Corresponding author. Tel +39.02.23699.739 ; Fax: +39.02.70636.400 e-mail: <u>erika.kozma@ismac.cnr.it</u>

Highlights

- Two new perylene diimide molecules were synthesized
- PDI-2 and PDI-3 were used as n-type components in solar cells
- Solar cells with P3HT exhibit efficiencies approaching 1%